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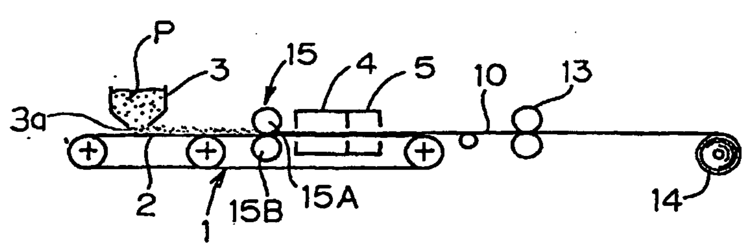
(54) Method of manufacturing porous metal sheet and metal sheet manufactured by this method

(57) Metal powders (P) are spread on a feeding belt (2) or a supporting sheet which is continuously fed. Then, the feeding belt or the supporting sheet on which the metal powders have been spread is passed between a pair of rolling rollers (150) to roll them at a required strength of pressure to leave fine gaps between the metal powders adjacent to each other. Thereafter, a resulting metal sheet (10) is passed through a sintering oven (4) to integrate the metal powders to each other so as to form a porous metal sheet having fine pores consisting of the gaps. It is possible to spread the metal powders on the rolling roller directly or to use a mixture of sublimable fine fragments and metal powders. Further, it is possible to form a solid metal sheet, namely, a metal sheet having no pores formed thereon, by setting the strength of pressure of the rolling roller to a high value.

Fig.1



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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of manufacturing a metal sheet which is preferably used as an electrode substrate of a battery and the metal sheet manufactured by the manufacturing method. More particularly, the present invention relates to a porous sheet formed of metal powders so that an active substance is filled into pores thereof. The porous sheet is preferably used as the electrode substrate of a nickel hydrogen battery, a nickel cadmium battery, a lithium primary battery, a lithium secondary battery, an alkaline dry cell, a fuel cell; and an electrode plate of various batteries, for example a battery for vehicles.

2. Description of the Related Art

As the porous metal sheets which are used as electrode substrates of batteries, the present applicant proposed various kinds of metal sheets formed by making a porous base plate such as a foamed material, a nonwoven sheet, a mesh material or a laminated sheet comprising two or more thereof electrically conductive and then electroplating them.

In manufacturing the porous metal sheets by the method, before electroplating the base plate such as the foamed material, the nonwoven sheet, the mesh material or the laminated sheet thereof, it is necessary to make them electrically conductive by a method selected from evaporating method, chemical plating method or carbon application method, which takes time and labor and costly. It is also necessary to burn the base plate to remove resinous materials after electroplating it and sinter the metal sheet. As a result, burnt-off portions of a resulting metal sheet are vented. An active substance cannot be filled thereinto.

In view of the problems, the present applicant proposed many methods of manufacturing porous metal sheets of metal powders.

In any of the above-described methods, using adhesive agent, fine metal powders are applied to entire surfaces including the inner surface of pores of the porous base plate so as to form an electrically conductive metal layer thereon. Then, the resinous material is removed and the fine metal powders are sintered to form metal sheets.

In the above-described conventional methods of manufacturing the porous metal sheet of fine metal powders, the fine metal powders are applied to the surface of the porous base plate. Thus, the size and shape of the pore of the porous metal sheet is restricted by the size and shape of the pore of the porous base plate. Thus it is difficult to form a pore smaller or greater than the pore of the porous base plate on the porous metal sheet and a pore whose shape is different from that of the pore of the porous base plate.

As one of the conditions required for a metal sheet to serve as the substrate of the electrode plate, it is necessary that the metal sheet is thin to accommodate a large amount of an active substance so as to improve the performance of a battery. But in the above-described conventional methods of manufacturing the porous metal sheet of fine metal powders, the thickness of the porous metal sheet is restricted by the thickness of the porous base plate. Hence it is difficult to manufacture the porous metal sheet having a thickness 1mm or less.

Further, adhesive agent is used in the above-described conventional methods. That is, fine metal powders are applied to the porous base plate by mixing them with the adhesive agent or after the adhesive agent is applied thereto. Thus when the adhesive agent is burnt off, together with the porous base plate in the removal of the resinous material and the sintering of the fine metal powders, large gaps are present between the fine metal powders adjacent to one another because the adhesive agent has been present therebetween. As such, it is difficult to control the shape and size of the pore. In addition, the conventional methods have a disadvantage that the porous metal sheet is formed in a large number of processes because the methods require the use of the adhesive agent.

Further, a solid metal foil is hitherto used as the substrate of the positive and negative electrodes of a lithium secondary battery. In this case, lithium ions are incapable of moving from the front surface of the electrode substrate to the rear surface thereof and vice versa. Therefore, in order to obtain a possible most uniform and thinnest active substance layer, the active substance is required to be applied to each surface of the substrate. In addition, because the surface of the electrode substrate is smooth, the active substance is liable to be separated from the electrode substrate.

In porous metal sheet whose shape is punching shape, lath-shape, mesh-shape, foamed material-shape, nonwoven sheet-shape and so on, lithium ions are capable of moving from the front surface of the electrode substrate to the rear surface thereof and vice versa, the thickness of the active substance can be controlled at both the front and rear surfaces of the electrode substrate by the porous metal sheet. Thus, research and development are being made to use such porous metal sheets as the electrode substrate of the lithium secondary battery. But the size of the solid portion of the porous metal sheet and the size of the pore thereof are not uniform. Therefore, the lithium ions are incapable of moving uniformly and sufficiently. Although it is preferable that the porous metal sheet has a large number of fine pores thereon to allow the lithium ions to move smoothly, the conventional porous metal sheet which satisfies such a demand has not been provided.

The electrode substrate of the lithium secondary

battery is required to have a thickness of 10μm - 30μm. But as described above, it is difficult for the conventional art to manufacture a conventional metal sheet having a thickness 1mm or less. That is, it is impossile to manufacture a metal sheet whose thickness is as small as a thin foil.

In recent years, portable equipment such as a video camera, a liquid crystal compact television, a CD player, and the like requiring high current have come into wide use. Thus, there is a growing demand for the development of a battery having a great discharge capacity and superior in discharge characteristic in a high load-applied state. In the conventional alkaline dry cell having a separator, pellets made from a positive electrode mixture are filled outside the separator and gel powdered zinc is filled inside the separator. As such, it is very difficult for the alkaline dry cell to have a great discharge capacity and have an improved discharge characteristic in a high load-applied state because the battery can has a limited space.

In order to solve the problem, researches are made on an alkaline dry cell whose negative electrode plate consists of a punching or expanding solid zinc foil or zinc foil and positive electrode plate consists of metal oxide. The negative electrode plate and the positive electrode plate are spirally coiled with a separator interposed to increase the area of the negative electrode plate and the positive electrode plate and the discharge capacity of the battery, and improve the discharge performance thereof in a high load-applied state. But the punching or expanding zinc foil has a problem that the open area ratio thereof is about 50% or less because pores are two-dimensional; pore-forming is carried out and thus a pore-formed portion is cut off and hence left parts of material are much; processing and material costs become high as the thickness of the zinc foil is increasingly thin; and strain and burr are liable to appear in the pore-forming process. Further, the solid zinc foil and the conventional porous metal sheet have problems similar to those of the lithium secondary battery.

Further, conventionally, the electrode of alkali secondary batteries such as the nickel hydrogen battery and the nickel cadmium battery is formed as follows; paste-like slurry of an active substance formed by mixing an active substance such as hydrogen-storing alloy powders or nickel hydroxide powders and electrically conductive agent comprising carbon, a binder and soon is applied to a collector such as punching metal, metal mesh, expanded metal. But the binder prevetns flow of electric current, thus making the electricity-collecting property in the thickness direction of the electrode worse.

SUMMARY OF THE INVENTION

The present invention has been developed to solve the problems and to improve a manufacturing method of a metal sheet made from metal powders. Accordingly, it is an object of the present invention to provide a metal sheet-manufacturing method capable of controlling the thickness thereof, the size of pores and the shape thereof as desired and eliminating the use of adhesive agent so as to manufacture the metal sheet in a simple process; and the metal sheet which is manufactured by the method.

It is another object of the present invention to provide an electrode which comprises a metal sheet into which a binder-unadded active substance consisting of powders can be charged and is superior in electricity-collecting performance.

In order to solve the problems there is provided a method of manufacturing a metal sheet comprising the steps of spreading metal powders on a feeding belt which is continuously fed; passing the feeding belt on which the metal powders have been spread through a pair of rolling rollers for controlling an area of contact between the metal powders adjacent to each other by rolling the metal powders on the feeding belt at a required pressure; and passing the metal powders through a sintering oven to fuse contact portions of the metal powders together after the rolling.

The feeding belt comprises a solid metal sheet, an inorganic sheet including a porous metal sheet or a laminated sheet composed of the solid metal sheet and the inorganic sheet including a porous metal sheet of a circulating driving device of belt conveyor type. For example, the feeding belt is SUS (310S). Metal powders spread on the feeding belt can be separated therefrom by sintering them to form into a sheet. That is, the metal powders can be formed into a metal sheet continuously with high efficiency by passing the feeding belt being continuously fed through the sintering oven.

As described above, because the metal powders are spread on the feeding belt and the feeding belt is passed between a pair of the rolling rollers to roll the metal powders at a required pressure. As a result, the spread metal powders are integrated with each other to form a metal sheet. Then, it is passed through the sintering oven as it stands and heated at a required temperature. Consequently, connected portions of the metal powders are fused together. As such, the metal sheet can be continuously formed.

The pressing force of the rolling roller is set to a small one to leave fine gaps between adjacent metal powders rolled by the rolling roller and the metal sheet works as a porous sheet by utilizing the fine gaps as pores.

That is, when the pressing force of the rolling roller is set to a small one, gaps can be left between the metal powders adjacent to each other to allow the porous metal sheet to have an innumerable number of fine gaps between the metal powders adjacent to each other. When the pressing force of the rolling roller is set to a large one, it is possible to obtain a solid metal sheet, namely, a metal sheet having no pores formed thereon.

The size of pores depends on the size of metal powders. That is, large pore is formed when the diameter of the metal powder is large, whereas a small pore is formed when the diameter of the metal powders is small. The metal powders having a diameter in the range of 0.1μm - 100μm can be preferably used.

Metals which can be used as the material of the metal sheet are not limited to a specific kind. The following substances can be preferably used: Ni, Cu, Al, Ag, Fe, Zn, In, Ti, Pb, V, Cr, Co, Sn, Au, Sb, C, Ca, Mo, P, W, Rh, Mn, B, Si, Ge, Se, La, Ga, and Ir. Each metal described aboves is used in the form of oxide and sulfide thereof and a substance or a mixture, including compounds of these metals. That is, Al, Ti, V, and the like which cannot be used in electroplating can be used. It is possible to use one kind of metal selected from these metals in the form of powders or a mixture of a plurality of these metals in the form of metal powders. It is desirable that metal powders of these metals do not interwine with one another and are dispersed favorably. That is, peripheral surfaces of the metal powders are desired not to be convex or concave so that they do not intertwine one another. Thus, it is preferable that the metal powders are spherical, dice-shape, square pillar, and columnar.

There is provided a method of manufacturing a metal sheet comprising the steps of feeding a supporting sheet continuously; spreading metal powders on the supporting sheet; feeding the supporting sheet on which the metal powders have been spread to a feeding belt; passing the supporting sheet between a pair of rolling rollers, together with the feeding belt; controlling an area of contact between the metal powders adjacent to each other by rolling the metal powders on the supporting sheet at a required pressure; and passing the metal powders through a sintering oven to fuse contact portions of the metal powders together after the rolling.

Similarly to the above method, a metal sheet can be obtained by spreading metal powders on the supporting sheet; passing the supporting sheet between a pair of the rolling rollers, with the supporting sheet placed on the feeding belt. Further, owing to the use of the supporting sheet, the resulting metal sheet can be separated from the supporting sheet more easily compared to the metal sheet formed on the feeding belt by directly spreading metal powders thereon.

There is preferably provided, the supporting sheet comprises an organic sheet including a solid resinous sheet, a three-dimensional reticulate resinous sheet and a porous fibrous resinous sheet, an inorganic sheet including a solid metal sheet and a porous metal sheet or a laminated sheet composed of a plurality of the sheets selected from the sheets.

Because a porous sheet consisting of a three-dimensional reticulate sheet or a porous fibrous sheet is used as the supporting sheet or the feeding belt, metal powders spread thereon drop from pores of the feeding belt or those of the supporting sheet. Consequently, portions corresponding to the pores thereof are formed as through-holes of the resulting metal sheet. The through-holes are larger than pores consisting of small gaps present between the metal powders adjacent to each other. As such, the metal sheet has the fine pores and the relatively large through-holes. Metal powders which have dropped from the pores of the feeding belt or those of the supporting sheet are collected to recycle them.

When a porous sheet is used as the feeding belt and the supporting sheet, pores of the porous sheet are circular, rhombic, polygonal or elliptic. By forming the pores having desired configurations on the feeding belt or the supporting sheet, a resulting porous metal sheet has pores whose configuration corresponds to that of the pores. For example, if the pores are circular, the formed sheet has punching hole-shape pores. If the pores are rhombic, the formed metal sheet is lath-shape.

There is porvided, sublimable fine fragments which are burnt off by heating are mixed with the metal powders or spread on the feeding belt or the supporting sheet before the metal powders are spread thereon; a mixture of the metal powders and the sublimable fine fragments spread on the feeding belt or the supporting sheet is rolled by the rolling roller; and after the rolling the sublimable fine fragments are burnt off in a resinous material-removing oven so that the metal sheet has pores which are formed in a portion where the sublimable fine fragments are burnt off.

In a case where some agent such as foaming agent which is decomposed to generate gas when it is heated is used as the sublimable fine fragments, a resulting porous metal sheet has through-holes formed by the generated gas. Further, the size of the through-holes can be controlled according to the diameter of particles of the sublimable fine fragments.

The supporting sheet is burnt off in the resinous material-removing oven. That is, the supporting sheet consisting of a resinous material is burnt off in the resinous material-removing oven.

When the supporting sheet consists of an inorganic sheet such as a metal sheet, there are two cases: In one case, it is not removed by heating but separated from a resulting metal sheet when it is discharged from the sintering oven, whereas in the other case, it is fed downstream, together with the metal sheet and wound as a coil. That is, the supporting sheet formed of a thin metal plate can be fed at a high speed and thus a high productivity can be obtained.

Further, the supporting sheet and the metal sheet formed of the metal powders may be laminated one on the other to manufacture a metal sheet having a laminated structure without burning it off in the resinous material-removing oven. Using various kinds of supporting sheets selectively, it is possible to manufacture metal sheets of various forms by laminating the desired supporting sheet and the metal sheet one on the other.

That is, the metal sheet include a solid metal plate or a solid metal foil; a metal sheet having a large number of pores formed thereon or a metal foil having a large number of pores formed thereon; a metal mesh; a metal screen; or/and a metal sheet plated three-dimensional reticulate foamed material, a porous fibrous resinous material, a mesh material or a laminate sheet of these materials at above-mentioned with a metal or evaporated a metal thereon, applied fine metal particles thereto or sprayed a metal thereto, and then removed resinous materials and sintered; a metal sheet formed of metal fibers; a metal sheet made of metal powders rolled by a pair of rolling rollers, at least one of which serves as a pattern roller; or a laminate sheet comprising these materials laminated one upon another and integrated with each other.

It is possible to laminate any one of the following metal materials on the upper and lower surfaces of the metal sheet manufactured by any one of the above-described methods of the present invention: The metal sheet manufactured by any one of the above-described methods of the present invention; a metal sheet or a metal foil having a large number of pores formed thereon; a metal mesh; a metal screen; a three-dimensional reticulate metal sheet or a nonwoven cloth-shaped metal sheet. In this case, the size of pores of the metal sheets positioned on one surface of the laminate sheet and the other surface thereof may be different from each other, and the open area ratio or/and the diameter of fiber of the porous metal sheet on one surface of the laminate sheet and the other surface thereof may be different from each other.

There is provided a method of manufacturing a metal sheet comprising the steps of spreading metal powders on a surface of a pair of rolling rollers rotating continuously; passing the metal powders between the rolling rollers for controlling an area of contact between the metal powders adjacent to each other by rolling the metal powders at a required pressure so as to form a metal sheet; and passing the metal sheet through a sintering oven to sinter the metal sheet.

That is, instead of rolling metal powders spread on the feeding belt or the supporting sheet by means of the rolling roller, the metal powders spread directly on the surface of the rolling roller are rolled at a required pressure by the rotation thereof at their contact portion to form a metal sheet. In this method, because the metal powders are fed out from the rolling roller in the form of a metal sheet, it is possible to move the metal sheet to a sintering oven without placing the metal sheet on the feeding belt or the supporting sheet. But in order to enhance productivity by increasing the pulling speed of the metal sheet, it is preferable to pass the metal sheet fed out from the rolling roller through the sintering oven, with the metal sheet placed on the feeding belt..

The pressing force of a pair of the rolling rollers is set to a small one to leave fine gaps between adjacent metal powders rolled by the rolling rollers and the metal sheet works as a porous sheet by utilizing the fine gaps as pores. That is, by adjusting the strength of the pressure of the rolling roller, it is possible to form a porous sheet having fine pores formed thereon or a solid sheet.

Sublimable fine fragments and the metal powders are spread on the surface of a pair of the rolling rollers; a mixture of the metal powders and the sublimable fine fragmetns are rolled by the rolling rollers to form the mixture into a metal sheet; and the metal sheet is passed through a resinous material-removing/metal powder-sintering oven to burn off the sublimable fine fragmetns and works as a porous sheet having pores which are formed in a portion where the sublimable fine fragments are burnt off.

By mixing the sublimable fine fragments and the metal powders with each other, it is possible to form a porous metal sheet having comparatively large pores according to the size of particles of the sublimable fine fragments and fine pores consisting of gaps formed between metal powders adjacent to each other.

Further, after a porous metal sheet having the fine pores formed thereon is obtained by the rolling rollers, it is fed to the sintering oven, together with the supporting sheet consisting of the porous metal sheet, with the porous metal sheet placed on the supporting sheet. This method allows a one-piece porous metal sheet comprising porous metal sheets of various forms laminated one on the other.

A surface of at least one of the rolling rollers on which the metal powders are spread is stepped at a position between a center and both edges thereof in its axial direction so that the metal powders are collected in a stepped center region thereof and pressed at a required pressure by the rolling rollers.

In a first example, a concave is formed in the center of one roller of a pair of rolling rollers in its axial direction, whereas the surface of the other roller is flat. In this construction, metal powders are collected in the concave of one roller; and metal powders spread on a convex formed at both sides of one roller are removed from the surface of one roller by sucking and the like. The metal powders collected in the concave are rolled by the flat rolling roller at a required pressure. In a second example, a concave is formed in the center of one roller of a pair of rolling rollers in its axial direction, and a convex which is inserted into the concave is formed in the center of the other roller in its axial direction. In this construction, metal powders collected in the concave are rolled by the convex of the other roller.

In a third example, a convex is formed in the center of the surface of one roller of a pair of rolling rollers in its axial direction, and the other roller is flat. In this construction, metal powders spread on the surface of the convex are rolled by the flat roller. In a fourth example, metal powders spread on the surface of a convex formed in the center of one roller of a pair of rolling rollers in its axial direction are rolled, with the convex fitted in a concave formed in the center of the other roller in its

axial direction.

In the above four examples, after a metal sheet is passed through the sintering oven, the metal sheet is passed through a cooling oven subsequently to the sintering oven. The rolling, the sintering, and the cooling may be repeated at a plurality of times. That is, it is possible to use the metal sheet formed by sintering metal powders as an electrode substrate. When the porous metal sheet does not have a desired strength, it is preferable to roll the obtained metal sheet again to increase the area of connection portions of metal powders adjacent to each other and the number of the connection portions thereof. If a great force is applied to the metal powders at a time, the resulting metal sheet may be meandered or cracked. Therefore, it is preferable to roll the metal powders at a low strength of pressure at a plurality of times.

The cooled metal sheet is separated from the feeding belt or the supporting sheet. When the supporting sheet consists of a metal sheet, it is possible to laminate it on a metal sheet manufactured to obtain a one-piece metal sheet, as described previously without separating it from the feeding belt or the supporting sheet.

Metal powders may be spread again on a surface of a metal sheet which is formed by the sintering, rolled, and a resulting metal sheet may be sintered. In this method, the thickness of the metal sheet can be increased to a desired one to enhance the tensile strength thereof.

There is provided a method of manufacturing a metal sheet, wherein pins are pierced into a metal sheet manufactured by a method at above-mentioned to form pores with burrs. According to the method, it is preferable that while the metal sheet is being fed, the metal sheet is passed between a pair of pins-provided rollers to form the pores with burrs.

It is possible that after the metal sheet is formed by the method at above mentioned, the metal sheet is wound as a coil and then, the pores with burrs are formed with the pins while it is being unwound from the coil or the pores with burrs are formed with the pins without winding it as a coil.

It is also possible to move pins-projected press plate toward the metal sheet being fed and away therefrom to form the pores with burrs (namely, burrs are formed around pores formed by pins). The force of holding the active substance can be increased by forming the pores with burrs.

There is provided a metal sheet manufactured by the method at above mentioned.

The metal sheet formed by using the sublimable fine fragments or/and a porous sheet as the feeding belt and the supporting sheet is punching shape, reticulates shape, honeycomb-shape, lath-shape, lattice-shape, expanded sheet-shape, screen-shape or lace-shape. That is, a metal sheet of desired shapes can be manufactured according to the shape of a pore of the sublimable fine fragment, the porous sheet.

It is preferable that the metal sheet has pore-unformed lead portions spaced at predetermined intervals.

Further there is provided a substrate for a battery electrode comprising a metal sheet at above mentioned.

Further, according to the present invention, there is provided an electrode for a battery in which an active substance is charged into pores of the substrate for the battery electrode, and an active substance layer is formed on at least one surface of the substrate of the battery electrode.

As the active substance, the following substances can be used: metals such as zinc, lead, iron, cadmium, aluminum, lithium, and the like; metal hydroxides such as nickel hydroxide, zinc hydroxide, aluminum hydroxide, iron hydroxide, and the like; complex oxides such as lithium dimanganese tetraoxide, lithium cobalt dioxide, lithium nickel dioxide, lithium divanadium tetraoxide and the like; metal oxides such as manganese dioxide, lead dioxide, and the like; electrically conductive polymers such as polyaniline, polyacethylene,and the like; hydrogen-storing alloy; carbon; and other substances. The kind is not limited.

Conventionally, when the active substance is charged into a substrate for a battery electrode, an electrically conductive material such as carbon powders and binder are added to the active substance. But according to the present invention, the active substance is used without adding the binder thereto.

In the case of the negative electrode of a nickel hydrogen battery, powders containing hydrogen-storing alloy as the main component are used as the active substance. In this case, the binder may be or may not be added to the active substance. The active substance containing hydrogen-storing alloy powders as the main component consists of hydrogen-storing alloy powders or a mixture of the hydrogen-storing alloy powders and a transition metal.

The metal sheet of the present invention has a large number of pores. Thus an active substance such as the hydrogen-storing alloy powders can be filled into the pores without binding it with binder and reliably held without dropping it from the metal sheet. The electricity-collecting performance of an electrode can be outstandingly enhanced by not adding the binder to the hydrogen-storing alloy. In particular, when the burr-provided pore is formed by piercing the metal sheet with pins, the hydrogen-storing alloy can be held by the burr on both sides of the metal sheet. Thus, an electrode holding the hydrogen-storing alloy at a high strength can be provided.

A surface of the active substance layer is covered partly or entirely with a transition metal. For example, in the case of the an electrode of hydrogen-storing alloy which is used for a nickel hydrogen battery, the surface of the hydrogen-storing alloy layer is covered with transition metals such as nickel powder and/or copper pow-

der. An active substance layer, for example, powder of a hydrogen-storing alloy layer can be held at a higher strength by coating the surface of the hydrogen-storing alloy layer with the transition metals.

It is preferable that on a metal sheet successively formed by the method at above mentioned, the metal sheet is successively fed downstream or after being wound as a coil the metal sheet is successively fed by uncoiling; then, an active substance is supplied successively to the metal sheet; then, it is pressurized to fill the active substance into pores of the metal sheet; and a layer of the active substance is formed on at least one surface of the metal sheet in a required thickness. That is, an electrode for a battery can be manufactured with high efficiency by supplying powder of the active substance at a required pressure after the process of forming metal powders into the metal sheet which constitutes an electrode substrate.

Further, according to the present invention, there is provided a battery comprising an electrode for a battery at above mentioned. As the battery, a nickel hydrogen battery, a nickel cadmium battery, a lithium primary battery, a lithium secondary battery, an alkaline dry cell, a fuel cell, and a battery for vehicles are exemplified.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view showing an apparatus for carrying out the method of a first embodiment of the present invention;
Fig. 2 is a schematic enlarged view showing a state of spread metal powders;
Fig. 3 is a schematic view showing an apparatus of a first modification of the first embodiment;
Fig. 4 is a schematic view showing an apparatus of a second modification of the first embodiment;
Fig. 5 is a schematic view showing an apparatus of a third modification of the first embodiment;
Fig. 6 is a schematic view showing an apparatus of a fourth modification of the first embodiment;
Fig. 7 is a schematic view showing an apparatus for carrying out the method of a second embodiment of the present invention;
Fig. 8 is a schematic view showing an apparatus of a first modification of the second embodiment;
Fig. 9 is a schematic view showing an apparatus for carrying out the method of a third embodiment of the present invention;
Fig. 10 is a plan view showing a metal sheet which is manufactured by the method of the third embodiment;
Figs. 11 (A) through 11 (D) are plan views each showing a supporting sheet which is used in the third embodiment;
Figs. 12 (A) and 12 (B) are schematic views each showing an apparatus for carrying out the method of a fourth embodiment of the present invention;
Fig. 13 is a schematic sectional view showing a metal sheet which is manufactured by the method of the fourth embodiment;
Figs. 14 (A), 14 (B), and 14 (C) are schematic sectional views each showing a through-hole-forming process of a modification of the fourth embodiment;
Fig. 15 is a schematic view showing an apparatus for carrying out the method of a fifth embodiment of the present invention;
Figs. 16 (A) and 16 (B) are schematic sectional views each showing a modification of a rolling roller;
Figs. 17 (A) and 17 (B) are schematic sectional views each showing another modification of a rolling roller;
Fig. 18 is a schematic view showing an apparatus of a modification of the fifth embodiment;
Fig. 19 is a schematic view showing an apparatus of sixth embodiment;
Fig. 20 is a schematic view showing an apparatus of a seventh embodiment of the present invention;
Fig. 21 is an enlarged sectional view of electrode manufactured by a method of the seventh embodiment;
Fig. 22 is a schematic view showing an apparatus of an eighth embodiment of the present invention;
Fig. 23 is an enlarged sectional view of electrode manufactured by a method of the eighth embodiment; and
Fig. 24 is an enlarged sectional view of electrode manufactured by a modified method of the eighth embodiment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The embodiments of the present invention will be described below in detail with reference to drawings.

First Embodiment

Fig. 1 shows the first embodiment. A circulating driving device 1 of belt conveyer type comprises an endless feeding belt 2; a storing hopper 3, for storing metal powders P, positioned over the feeding belt 2 and at the upstream side thereof; the rolling rollers 15 positioned at the intermediate region to pass the feeding belt 2 between an upper roller 15A and a lower roller 15B of the rolling rollers 15; and a sintering oven 4 and a cooling oven 5 both positioned at the downstream side thereof to pass the feeding belt 2 therethrough.

The feeding belt 2 is SUS (310S) which is flexible. An unshown metering controller is installed on a discharge opening 3a positioned at the lower end of the storing hopper 3 so that the metal powders P can be spread on the upper surface of the feeding belt 2 at a required density and thickness. The metal powders P have diameters in the range of 0.1μm - 100μm and are preferably, spherical, flake-shaped or spike-shaped.

As described above, because the metal powders P spread on the feeding belt 2 are in an uncompressed state, as shown in Fig. 2, entire surfaces of adjacent metal powders are not in contact with each other, but partly in contact with each other. More specifically, they are in a dot contact state or in a line contact state, thus forming a pore C (gap) between the adjacent metal powders P.

In this construction, the metal powders P are integrated with each other and become sheet-shaped by rolling them while they are passing between a pair of the upper roller 15A and the lower roller 15B of the rolling rollers 15, together with the feeding belt 2. At this time, the contact area of the adjacent metal powders P is controlled and the size of the gap between the adjacent metal powders P is adjusted by adjusting the strength of pressure. That is, when the metal powders P are rolled at a high strength of pressure, a resulting metal sheet becomes solid, whereas when the metal powders P are rolled at a low strength of pressure, a resulting metal sheet has comparatively many fine pores. The thickness of the resulting metal sheet is adjusted to a required one by adjusting the strength of pressure.

By passing the metal powders P between the upper roller 15A and the lower roller 15B of the rolling rollers 15, they are formed as a metal sheet shape on the feeding belt 2, and then, a material shaped into a metal sheet is passed through the sintering oven 4 to sinter it by heating it at a required temperature. As a result, connected portions of the adjacent metal powders P are fused together to form a metal sheet 10. When pores C consisting of gaps between the adjacent metal powders P are still present in rolling the metal powders P, the pores C are present between the metal powders P integrated with each other by the sintering to form the metal sheet 10 continuously having a fine porous structure. That is, after the porous metal sheet 10 is obtained by sintering the metal sheet in the sintering oven 4, the porous metal sheet 10 is cooled in the cooling oven 5 at a required temperature.

After the metal sheet 10 is discharged from the cooling oven 5, the metal sheet 10 is separated from the surface of the feeding belt 2 and then, tempered by passing it between a pair of skin pass rollers 13. Then, the metal sheet 10 is wound as a coil 14.

Experiment 1

Using the apparatus shown in Fig. 1, the metal sheet 10 was manufactured. That is, electrolytic copper powders whose average diameter was 15μm - 60μm were spread on the feeding belt 2 from the hopper 3. The copper powders were rolled at a compressive load of four tons to form them into a metal sheet shape. Then, a material shaped into a metal sheet was sintered in a non-oxidizing atmosphere in the sintering oven 4 at 950° C for 30 seconds. The metal sheet was then cooled in the cooling oven 5 to 50° C. When the resulting metal sheet 10 was discharged from the cooling oven 5, it was separated from the feeding belt 2. While the metal sheet 10 was being passed between a pair of the skin pass rollers 13, a load of six tons was applied thereto. The obtained copper sheet 10 was 14μm in thickness; 7.7% in open area ratio; 115g/m^2 in weight per area; 1.98kgf/20mm in tensile strength.

Fig. 3 shows a first modification of the first embodiment. Metal powders P spread on the feeding belt 2 are rolled by the rolling rollers 15 to form them into a metal sheet shape. A material shaped into a metal sheet is separated from the feeding belt 2. Thereafter, only the material shaped into a metal sheet is passed through the sintering oven 4 and the cooling oven 5. That is, after the metal powders P are rolled by the rolling rollers 15 to form them into the metal sheet, the metal sheet can be fed by pulling it without supporting it by means of the feeding belt 2. Thus, it is unnecessary to pass the metal sheet through the sintering oven 4 and the cooling oven 5 with supporting it by means of the feeding belt 2.

Fig. 4 shows a second modification of the first embodiment. One roller 16 of the rolling rollers 15' is used as a driving roller for circulating the feeding belt 2. The other roller 15A' of the rolling rollers 15' confronts the driving roller 16. In this modification, metal powders P spread on the upper surface of the feeding belt 2 from the hopper 3 is fed between the roller 16 of the rolling rollers 15' and the roller 15A' thereof to roll them at a required pressure to form the metal powders P into a metal sheet shape. A material shaped into a metal sheet is moved downward from the rolling rollers 15'. A feeding belt 2' of a circulating driving device 1' is located horizontally below the rolling rollers 15'. The sintering oven 4 and the cooling oven 5 are positioned at the downstream side of the circulating driving device 1' to pass the feeding belt 2' therethrough.

In this construction, the material shaped into a metal sheet fed downward from the rolling rollers 15' is fed into the sintering oven 4 with the feeding belt 2' to sinter it. Then, the resulting metal sheet 10 is cooled in the cooling oven 5. Then, it is separated from the feeding belt 2' and is passed between a pair of the skin pass rollers 13. As the last process, it is wound as a coil 14.

Fig. 5 shows a third modification of the first embodiment of the present invention. In the third modification, in the region downstream of the feeding belt 2 of the circulating driving device 1, second rolling rollers 6, a second sintering oven 7, and a second cooling oven 8 are arranged along the feeding path of the metal sheet 10. In the region downstream from the second cooling oven 8, third rolling rollers 9, a third sintering oven 11, and a third cooling oven 12 are arranged. A pair of the skin pass rollers 13 is installed downstream from the third cooling oven 12. The resulting metal sheet 10 has a high strength owing to a rolling, a sintering, and a cooling that are repeated at a plurality of times. When a great pressure is applied to the metal sheet 10 at a time when it is rolled, it may be damaged, cut or meandered.

Thus, it is preferable to roll the metal sheet 10 at a plurality of times as shown in a fourth modification. However, even in the rolling of the metal sheet 10 at a plurality of times, in order to manufacture the metal sheet 10 as a porous sheet, the strength of pressure is adjusted to keep the fine pores left between the adjacent metal powders P.

Fig. 6 shows the fourth modification of the first embodiment. The long circulation driving device 1 of belt conveyor type is provided. Metal powders P are spread on the feeding belt 2 from the first hopper 3A. After they are rolled by first rolling rollers 15, they are passed through a first sintering oven 4A and a first cooling oven 5A to form a metal sheet. Then, the metal powders P are spread on the metal sheet from a second hopper 3B, and the metal sheet is then passed through second rolling rollers 150 and a second sintering oven 4B, with the metal powders P placed on the metal sheet. The resulting metal sheet 10 is cooled in a second cooling oven 5B. The metal sheet 10 having a large thickness can be obtained by repeating the spreading, rolling, sintering, and cooling of the metal powders P at a plurality of times.

As described above, after repeating the spreading, rolling, sintering, and cooling of the metal powders P at a plurality of times on the feeding belt 2, the resulting metal sheet is separated from the feeding belt 2 and passed between the rolling rollers 6, similarly to the first embodiment, and then, the resulting metal sheet is sintered again in the second sintering oven 7 and cooled again in the second cooling oven 8 to increase the strength thereof. After that, the metal sheet 10 is passed through the skin pass rollers 13 and wound as a coil 14.

Second Embodiment

Fig. 7 shows the second embodiment. In the second embodiment, the metal powders P are not spread on the feeding belt 2 of the circulating driving device 1 directly, but a supporting sheet 20 made of organic resin is used. That is, the supporting sheet 20 is continuously unwound from a coil 21 and fed to the upper surface of the feeding belt 2 of the circulating driving device 1 downstream by the guidance of a guide roller 22. In the region upstream from the circulating driving device 1, the metal powders P are spread on the supporting sheet 20 from the hopper 3.

The supporting sheet 20 on which the metal powders P are spread is rolled by rolling rollers 15 consisting of upper and lower rollers sandwiching the supporting sheet 20 therebetween. After that, with transferred on the feeding belt 2, the supporting sheet 20 is sequentially passed through a resinous material-removing oven 23, a sintering oven 4, and a cooling oven 5. The metal powders P are rolled by the rolling rollers 15 at a required pressure, with fine pores left between the adjacent metal powders P. Then, the supporting sheet 20 is burnt off in the resinous material-removing oven 23. Then the metal powders P are sintered in the sintering oven 4 to form the metal sheet 10. Then, the metal sheet 10 is cooled in the cooling oven 5. When the metal sheet 10 is discharged from the cooling oven 5, it is separated from the feeding belt 2 and passed between a pair of the skin pass rollers 13. Finally, it is wound as a coil 14.

Fig. 8 shows a first modification of the second embodiment. In the first modification, an inorganic supporting sheet 20' which is not removed when it is heated in the sintering oven is used as the supporting sheet. In using the inorganic supporting sheet 20', the metal sheet 10 is separated from the supporting sheet 20' when the supporting sheet 20' is separated from a feeding belt 2 of a circulating driving device 1 to feed only the metal sheet 10 to the rolling rollers 6, the second sintering oven 7, and the second cooling oven 8, and a pair of the skin pass rollers 13. The obtained metal sheet 10 is wound as a coil 14.

In using the inorganic supporting sheet 20' which is not removed when it is heated, it is possible that after the metal sheet 10 is formed of metal powders, it is not separated from the supporting sheet, but fed continuously, together with the supporting sheet to wind them as the coil 14. In this case, by using a thin solid metal sheet as the supporting sheet, it is possible to obtain a metal sheet consisting of the solid metal sheet and the porous metal sheet laminated thereon.

In the first modification shown in Fig. 8, the solid metal sheet is used as the supporting sheet 20', but instead, it is possible to use a metal sheet with holes such as a punching metal and the like, a three-dimensional reticulate porous metal sheet, a porous fibrous metal sheet or the porous metal sheet formed by the apparatus shown in Fig. 1 to obtain a porous metal sheet consisting of any one of the above porous metal sheets and the porous metal sheet laminated thereon.

Third Embodiment

Fig. 9 shows the third embodiment. The third embodiment is different from the second embodiment in that a supporting sheet 30 which has holes formed thereon and can be burnt off is used in the third embodiment. The process of manufacturing the porous metal sheet of the third embodiment is similar to that of the second embodiment. Thus, the parts of the apparatus of the third embodiment are denoted by the same reference numerals as those of the apparatus of the second embodiment.

That is, as shown in Fig. 11 (A), a resinous sheet is used as the supporting sheet 30. Circular punched holes 30a are formed on the resinous sheet 30 at regular intervals lengthwise and widthwise. Therefore, when the metal powders P are spread on the supporting sheet 30 from the hopper 3, the metal powders P drop through the circular holes 30a, thus accumulating on the upper surface of the supporting sheet 30, with holes

present at required pitches on the upper surface thereof.

The metal powders P which have dropped through the circular holes 30a are stored in a metal powder receiver 31 installed in confrontation with the hopper 3 to recycle them.

As described above, the metal powders P spread over the supporting sheet 30 having the holes 30a formed thereon are rolled by the rolling rollers 15 at a required pressure. Then, a metal sheet consisting of the metal powders P is fed downstream, with the metal sheet placed on a feeding belt 2 of a circulating driving device 1 to pass it through a resinous material-removing oven 23, together with the supporting sheet 30 to remove the supporting sheet 30 at a required temperature by heating it. Then, the metal sheet is fed into the sintering oven 4 to sinter it by heating it at a required temperature.

Similarly to the second embodiment, after the metal sheet is passed through the sintering oven 4 and the cooling oven 5, it is separated from the feeding belt 2. After that, the metal sheet is passed between a pair of the skin pass rollers 13 and then wound as a coil 14.

Similarly to the first and second embodiments, in the third embodiment, in the portion of a metal sheet 10' corresponding to the circular holes (30a)-unformed portion of the supporting sheet 30, contact surfaces of the spread metal powders P are integrated with each other to form a fine porous structure by rolling them by the rolling rollers 15 at a controlled strength of pressure, whereas in the portion thereof corresponding to the circular hole (30a)-formed portion of the supporting sheet 30, pores consisting of comparatively large through-holes are formed. That is, as shown in Fig. 10, it is possible to continuously manufacture the porous metal sheet 10' having two kinds of pores, namely, fine pores C1 consisting of gaps present between the adjacent metal powders P and pores C2 consisting of large through-holes corresponding to the circular holes 30a.

In the third embodiment, because the supporting sheet having circular holes shown in Fig. 11 (A) formed thereon is used, the pores C2 consisting of large through-holes formed on the porous metal sheet 10' are circular. Besides it is possible to use the supporting sheet 30 having rectangular holes formed thereon as shown in Fig. 11 (B); the supporting sheet 30 having polygonal holes formed thereon as shown in Fig. 11 (C); or the supporting sheet 30 having rhombic holes formed thereon as shown in Fig. 11 (D). In these cases, it is possible to obtain a porous metal sheet having the pores C2 consisting of large through-holes rectangular, polygonal or rhombic formed thereon.

Fourth Embodiment

In the fourth embodiment shown in Figs. 12 and 13, sublimable fine fragments are mixed with metal powders P. When an apparatus similar to that of the first embodiment is used, the mixture is spread on a feeding belt 2 of a circulating driving device 1 of belt conveyor type, then, passed between rolling rollers 15 to roll it at a required strength of pressure, and thereafter passed through the resinous material-removing oven to burn off the sublimable fine fragments 50 to form comparatively large pores.

As the sublimable fine fragments, for example resinous spherical fragments (so-called bead-shape fragments), resinous cubic fragments, resinous rectangular fragments or resinous ultra-fine particles and the like which are burnt off by heating can be used.

More specifically, as shown in Fig. 12 (A), in the fourth embodiment, a hopper 3 storing metal powders P and a hopper 51 storing sublimable fine fragments 50 are installed above a mixing hopper 52. Similarly to the hopper 3 of the first embodiment, the mixing hopper 52 is located above the feeding belt 2 of the circulating driving device 1. An agitator 53 for mixing the metal powders P and particles of the sublimable fine fragments 50 with each other substantially uniformly is provided inside the mixing hopper 52.

The metal powders P and the particles of the sublimable fine fragments 50 are mixed with each other. After the mixture is spread on the upper surface of the feeding belt 2 of the circulating driving device 1, the mixture is passed between rolling rollers 15 to roll it at a required strength of pressure. Then, the mixture is passed through a resinous material-removing oven 23 and a sintering oven 4, with the feeding belt 2 to heat it. As a result, the particles of the sublimable fine fragments 50 sublimate. Consequently, as shown in Fig. 13, the portions of a resulting porous metal sheet in which the particles of the sublimable fine fragments 50 have been present are formed as pores C3. That is, a resulting metal sheet 10" has fine pores C1 and the comparatively large pores C3 formed in the portion where the particles of the sublimable fine fragments 50 have been present. The pores C3 consist of not only through-holes, but also pores present randomly in the thickness direction of the metal sheet 10".

The pores C3 having various sizes can be formed by changing the size of the particles of the sublimable fine fragments 50. Further, the pores C3 having various sizes and shapes can be easily formed by mixing the particles of the sublimable fine fragments 50 having different sizes and shapes with the metal powders P.

It is preferable to cool the metal sheet after the particles of the sublimable fine fragments 50 are burnt off and the metal powders P are sintered and then, roll, sinter, and cool it repeatedly, similarly to the first through third embodiments.

As shown in Fig. 12 (B), the hopper 51 storing the sublimable fine fragments 50 may be installed above the feeding belt 2 and at the upstream side of the feeding belt 2, and the hopper 3 storing the metal powders P may be installed above the feeding belt 2 and downstream from the hopper 51 so that after the particles of

the sublimable fine fragments 50 are spread on the feeding belt 2, the metal powders P are spread thereon. In this construction, the metal powders P are spread in gaps between adjacent particles of the sublimable fine fragments 50. Thus, the metal powders P and the particles of the sublimable fine fragments 50 are mixed with each other, similarly to the above-described embodiment shown in Fig. 12 (A).

When blowing agent which is decomposed to generate gas is used as the sublimable fine fragments 50, through-holes are formed by the generated gas. That is, as shown in Fig. 14 (A), by mixing the sublimable fine fragments 50 consisting of comparatively large particles with the metal powders P, gas is generated when the mixture is heated, as shown in Fig. 14 (B). As a result, through-holes C4, namely, pores penetrating a resulting porous metal sheet vertically are formed in the portion where the sublimable fine fragments 50 have been present, as shown in Fig. 14 (C). In this case, a resulting porous metal sheet has pores consisting of comparatively large through-holes and fine pores.

Fifth Embodiment

In Fig. 15 showing the fifth embodiment of the present invention, metal powders P are directly spread on rolling rollers 150 consisting of upper and lower rollers 150A and 150B from a hopper 3, and rolled at a required strength of pressure in a minimum gap X between the upper and lower rollers 150A and 150B by the rotation thereof to form fine gaps between adjacent metal powders P, similarly to the first through fourth embodiments. The fine gaps are formed as pores of a resulting porous metal sheet.

That is, in the fifth embodiment, the rolling rollers 150 consisting of upper and lower rollers 150A and 150B is positioned in such a manner that they do not sandwich the feeding belt 2 therebetween but they are positioned above the circulating driving device 1; the hopper 3 is positioned above the rolling rollers 150; and the metal powders P are continuously spread on the upper surface of the roller 150A from the hopper 3.

The circulating driving device 1 is positioned below the rolling rollers 150. The metal sheet 10' fed downward from the rolling rollers 150 is placed on the feeding belt 2 of the circulating driving device 1 to pass it through the sintering oven 4 and the cooling oven 5, together with the feeding belt 2. Then, the metal sheet 10' is separated from the feeding belt 2 and then passed between a pair of skin pass rollers 13. Thereafter, the metal sheet 10' is wound as a coil 14.

As apparent from the above description, the spreading of the metal powders P directly on the surface of the rolling roller 150 allows them to be rolled by the rollers 150A and 150B of the rolling roller 150 and fed from the rolling roller 150 in the form of the metal sheet 10'. Thus, the metal sheet 10' can be fed without the feeding belt or the supporting sheet.

In the fifth embodiment shown in Fig. 15, the rollers 150A and 150B whose surfaces are flat are used, but a construction described below may be adopted: The surface of the rollers 150A and/or 150B are stepped at a position between the center and both ends thereof in its axial direction so that the metal powders P spread on the roller 150A are collected in a stepped center region and pressed at a required pressure by the rollers 150A and 150B, as shown in Figs. 16 (A), 16 (B), 17 (A), and 17 (B).

More specifically, in the rolling roller 150 shown in Fig. 16 (A), a concave 150a is formed in the center of the roller 150A in its axial direction, whereas the surface of the roller 150B is flat. In this construction, the metal powders P are collected in the concave 150a of the roller 150A; and the metal powders P spread on a convex 150b formed at both sides of the roller 150A are removed from the surface of the roller 150A by sucking. The metal powders P stored in the concave 150a are rolled by the flat roller 150B at a required pressure in the region in which they contact the flat roller 150B. In the construction, a strength of pressure by the rolling rollers 150 can be easily controlled by controlling the depth of the concave 150a and the spread amount of the metal powders P, and further, it is easy to control the width of the metal sheet which can be formed by rolling the metal powders P.

In the rolling rollers 150 shown in Fig. 16 (B), the concave 150a is formed in the center of the rolling roller 150A in its axial direction, and a convex 150c which is inserted into the concave 150a is formed in the center of the rolling roller 150B in its axial direction. In this construction, the metal powders P collected in the concave 150a are rolled by the convex 150c of the rolling roller 150B, with the convex 150c fitted in the concave 150a. Similarly to the construction shown in Fig. 16 (A), the metal powders P can be rolled at a desired strength of pressure by setting the condition of the contact between the concave 150a and the convex 150c as desired, and further, it is easy to control the width of the metal sheet which can be formed by rolling the metal powders P.

In the rolling rollers 150 shown in Fig. 17 (A), a convex 150d is formed in the center of the surface of the rolling roller 150A in its axial direction, and the rolling roller 150B is flat. In this construction, metal powders P spread on the surface of the convex 150d are rolled by the flat roller 150B. In this construction, when the metal powders P are spread on the surface of the rolling roller 150A, the metal powders P on the surface of the convex 150d can be rolled without removing the metal powders P dropped to a step portion 150e positioned below the convex 150d and at both sides thereof by sucking.

In the rolling rollers 150 shown in Fig. 17 (B), metal powders P spread on the surface of a convex 150d formed in the center of the rolling roller 150A in its axial direction are rolled, with a convex 150d fitted in a concave 150f formed in the center of the rolling roller 150B in its axial direction.

Modification of Fifth Embodiment

In a modification of fifth embodiment shown in Fig. 18, after a mixture of metal powders P and sublimable fine fragments 50 put into a hopper 52 is agitated by an agitator 53, the mixture is spread on a rolling roller 150 directly from the hopper 52. Then, the rolling roller 150 rolls the mixture, thus forming it into a sheet. The metal sheet fed downward from the rolling roller 150 is fed to a feeding belt 2 of the circulating driving device 1 positioned below the rolling roller 150. Then, the metal sheet is passed through a resinous material-removing oven 23, together with the feeding belt 2 to burn off the sublimable fine fragments 50 to form comparatively large three-dimensional pores. After the metal sheet is passed through a sintering oven 4 and a cooling oven 5, it is separated from the feeding belt 2. Then, the metal sheet is passed between a pair of skin pass rollers 13 and wound as a coil 14.

Experiment 2

80 parts by weight of copper powders (average diameter: 15μm - 60μm) obtained by electrolysis and 20 parts by weight of sublimable fine fragments (particle diameter: 15μm - 20μm) were mixed with each other. The mixture was spread on the surface of the rolling roller 150 to roll it at a load of eight tons so as to form the mixture into a copper sheet. The copper sheet was fed to the feeding belt 2 and then heated at 500° C in an atmospheric environment in the resinous material-removing oven 23 to burn off the sublimable fine fragments. Then, the copper sheet was sintered in the sintering oven 4 at 950 ° C for thirty seconds in a non-oxidizing atmosphere. Then, the copper sheet was cooled in the cooling oven 5, and then separated from the feeding belt 2. Then, it was passed between a pair of the skin pass rollers 13 to temper it at a load of eight tons and wound as a coil. The obtained copper sheet was 17μm in thickness; 24.1% in open area ratio; 115g/m^2 in weight per area; and 1.67kgf/20mm in tensile strength.

Sixth Embodiment

Fig. 19 shows the sixth embodiment. In the sixth embodiment, before a metal sheet 10 manufactured in previous processes is passed between a pair of skin pass rollers 13, it is passed between lead portion-forming rollers 70A and 70B. A convex 71 is formed on the rollers 70A and 70B at both ends and the center thereof in the lengthwise (axial) direction thereof such that the convex 71 of the roller 70A and that of the roller 70B are radially spaced at a predetermined interval and coincident with each other in the lengthwise (axial) direction thereof. Thus, when the metal sheet 10 is passed between the rollers 70A and 70B, fine pores of the metal sheet 10 are crushed by the pressing force of the upper and lower convex 71. As a result, the crushed portion of the metal sheet 10 becomes solid. The solid portion of the metal sheet 10 is used as a lead portion 72. When the metal sheet 10 is used as an electrode substrate of a battery, the lead portion 72 performs an electric current collecting function.

The method of manufacturing the porous metal sheet of the present invention is not limited to the embodiments, but it is possible to use the manufactured metal sheet as a supporting sheet so that metal powders are spread on the supporting sheet and the porous metal sheet is repeatedly used until the porous metal sheet has a desired thickness and strength.

Further, a solid metal sheet, namely, a metal sheet having no pores formed thereon may be formed by rolling the metal powders P at a high strength of pressure.

Figs. 20 and 21 show a seventh embodiment. In the seventh embodiment, a metal sheet 10 formed by the method of the first embodiment shown in Fig. 1 is wound as a coil 14; the metal sheet 10 is unwound from the coil 14 and fed successively to pass between pin-provided rollers 100A and 100B; pores with burrs 110 are formed on the metal sheet 10 by pins 101 at both sides thereof; and an active substance , for example containing hydrogen-storing alloy as its main component, is supplied to the metal sheet 10 while it is being fed successively to form an electrode.

That is, as shown in Fig. 20, in a process similar to that of the first embodiment, the metal sheet 10 is tempered by passing between a pair of skin pass rollers 13 to prepare the metal sheet 10 and wound as the coil 14. The metal sheet 10 unwound from the coil 14 is successively fed and guided vertically between the pins-provided rollers 100A and 100B so that the pores with burrs 110 are formed on the metal sheet 10 by the pins 101 at both sides thereof. Then, powders (for example, mixed powders of hydrogen-storing alloy powders and nickel powders) 82 of an active substance stored in a hopper 81 positioned at both sides of the metal sheet 10 and above rollers 80A and 80B are supplied to both surfaces of the metal sheet 10 and between the rollers 80A and 80B.

The mixed powder 82 are filled into the pores with burrs 110 of the metal sheet 10 by the pressing force of the rollers 80A and 80B and held on both surfaces of the metal sheet 10 by burrs 111 to form active substance layers (for example, hydrogen-storing alloy) 85A and 85B having a required thickness.

Then, the metal sheet 10 on which the active substance layers are formed is passed through a sintering oven 86 to sinter it at a non-oxidizing atmosphere. Then it is passed through a cooling oven 87 to cool it. Finally, it is tempered at a required load by passing it between a pair of skin pass rollers 88. An electrode 90(for example, hydrogen-storing alloy) thus formed is wound successively as a coil 91.

Experiment 3

A nickel sheet 10 formed by rolling metal powders by the skin pass roller 13 had a thickness of 25μm and a width of 100mm. Pores were formed on the metal sheet 10 with the pins 101 installed on the rollers 100A and 100B at intervals of 0.2mm to provide burrs having a height of 0.6mm. The diameter of the pins 101 was 0.7mm. In the state in which the pores with burrs were formed by piercing the metal sheet 10 with the pins 101, the open area ratio of the metal sheet 10 was 54.8% (plane). The mixed powders 82 which were supplied to the metal sheet 10 were spherical with a powder diameter of 60μm - 80μm. The mixed powders 82 were formed by mixing 18 parts by weight of spherical hydrogen-storing alloy powders of AB_5 type with two parts by weight of nickel powders having an average powder diameter of 2.5μm. The mixed powder 82 was so supplied to both surfaces of the metal sheet 10 that 900g/m^2 (90g/m) was applied to each surface. Then, a load of five tons was applied to the metal sheet 10 by the rollers 80A and 80B of Ø 150mm to roll it at a line speed 1m/min. Then, the metal sheet 10 was sintered at 950° C for two minutes in the sintering oven 86 having a non-oxidizing atmosphere. Finally, the metal sheet 10 was tempered at a load of five tons by passing it between a pair of the skin pass rollers 88 to prepare the electrode 90 of the hydrogen-storing alloy having a thickness of 0.3mm.

A binder was not added to the mixed powders of the hydrogen-storing alloy powders and the nickel powders which were supplied to the metal sheet 10. But pores with burrs 110 were formed on the metal sheet at intervals of as small as 0.2mm and the burrs 111 having a height of 0.6mm projected at both sides of pores with burrs. Thus, the mixed powder was firmly held on the metal sheet 10.

As described above, because the binder is not added to the mixed powder, the flow of electric current was not inhibited by the binder. Further, because nickel powders were added to the mixed powder instead of carbon which was conventionally used as an electrically conductive material, the electrode 90 had a high degree of electricity-collecting performance.

Figs. 22 and 23 show an eighth embodiment. In the eighth embodiment, electrodes are successively formed by supplying an active substance prepared by mixing hydrogen-storing alloy powders and nickel powders with each other to a metal sheet 10' which has great pores C2 and fine pores C1 and which is formed by the method of the third embodiment shown in Fig. 9

That is, as shown in Fig. 22, tempering is performed by passing metal powders between a pair of skin pass rollers 13 to form the metal sheet 10' and then it is successively fed and guided vertically to a hopper 81 positioned above rollers 80A and 80B positioned at both sides of the metal sheet 10', without winding it as a coil. Mixed powder 82 of hydrogen-storing alloy powders and nickel powders stored in the hopper 81 are supplied to both sides of the metal sheet 10' and between the rollers 80A and 80B. The supplied mixed powders 82 are filled into the pores C1 and C2 by the pressing force of the rollers 80A and 80B and fixedly attached to both surfaces of the metal sheet 10' to form layers 85A and 85B having a required thickness. Then, the metal sheet 10' is passed through a sintering oven 86 to sinter it in non-oxidizing atmosphere and passed through a cooling oven 87 to cool it. Finally, it is passed between a pair of a skin pass roller 88 to temper it at a required load. An electrode 90 (shown in Fig. 21) of the hydrogen-storing alloy thus formed is successively wound as a coil 91.

Experiment4

In a nickel metal sheet 10' formed by rolling metal powders by the skin pass roller 13, the diameter of the great pore C2 was 1.8mm; open area ration was 47.0%; and thickness was 25μm. The mixed powders 82 which were supplied to the metal sheet 10' was prepared by mixing 18 parts by weight of 60μm - 80μm of the hydrogen-storing alloy powders of AB_2 type with two parts by weight of nickel powders having an average powder diameter of 2.5μm. The mixed powders 82 were supplied to both surfaces of the metal sheet 10' at 540g/m^2 on each surface. Then, the metal sheet 10' was pressurized by the rollers 80A and 80B of Ø 150mm at a load of five tons to roll it at a line speed of 1m/min. Then, the metal sheet 10' was sintered in the sintering oven 86 having non-oxidizing atmosphere at 950° C for two minutes. Finally, the sintered metal sheet 10' was rolled by the skin pass rollers 88 at a load of five tons to form the electrode 90 of the hydrogen-storing alloy having a thickness of 0.18mm.

In the electrode 90 of the hydrogen-storing alloy manufactured as described above, because binder is not added thereto, the flow of electric current is not inhibited. Further, because nickel powders are added thereto instead of carbon which is conventionally used as an electrically conductive material, the electrode 90 has a high degree of electricity-collecting performance.

A method of successively manufacturing electrodes such as an electrode of the hydrogen-storing alloy after manufacturing the metal sheet is not limited to the above-described method. That is, it is possible to successibley manufacture electrodes by uncoiling a metal sheet, similarly to the seventh embodiment after performing the method of the second, fourth, fifth, and sixth embodiment, and then filling an active substance into pores thereof while it is being fed, or similarly to the eight embodiment, filling the active substance into pores of the metal sheet while it is being fed successively, without coiling the metal sheet. Further, it is possible to mix other transition metals, for example, copper powders with the hydrogen-storing alloy powders, instead of nickel powders. In addition, two and more transition metals, for example, nickel powders and cop-

per powders may be mixed with the hydrogen-storing alloy powders. Further, only the hydrogen-storing alloy powders may be used singly. The shape of the transition metal is not limited to the shape of powders.

For example, the sublimable fine fragments of the fourth embodiment shown in Fig. 12 are mixed with mixed powders and supplied to a feeding belt. Then, the hydrogen-storing alloy powders are supplied to a metal sheet 10" having pores formed by burning off the sublimable fine fragments. In this manner, an electrode of the hydrogen-storing alloy may be successively manufactured.

Experiment 5

The nickel metal sheet 10" having a thickness of 25μm and open area ratio of 35% was prepared by the method of the fourth embodiment shown in Fig. 12. Hydrogen-storing alloy powders similar to that of experiment 4 were supplied to both surfaces of the metal sheet 10". Then, it was pressurized at a load of five tons, and then sintered in a sintering oven having non-oxidizing atmosphere at 950° C for two minutes. Finally, the sintered metal sheet was tempered by a skin pass rollers to form an electrode of the hydrogen-storing alloy having a thickness of 0.18mm.

In the electrode of the hydrogen-storing alloy thus prepared, because the metal sheet has pores formed by the sublimable fine fragments and fine pores between metal powders, the pores were filled with the hydrogen-storing alloy powders. Further, a thin layer of the hydrogen-storing alloy powders was reliably fixed to both surfaces of the metal sheet by the sintering the pressure application by means of the skin pass roller.

It is possible that after the hydrogen-storing alloy powders are supplied to the metal sheet to fill the pores and both surfaces thereof with the hydrogen-storing alloy powders as described above, powders of a transition metal such as nickel are supplied to the surface of the hydrogen-storing alloy layers 85A and 85B at both sides of the metal sheet to form a transition metal layer 95 as shown in Fig. 24. The hydrogen-storing alloy powders can be held at a high strength by providing the transition metal layer 95.

The metal which is supplied to the surface of the hydrogen-storing alloy layers 85A and 85B is not limited to nickel powders, but powders of a transition metal such as copper or mixed powders of nickel powders and copper powders may be used. Further, the hydrogen-storing alloy layers may be formed on only one surface of the porous metal sheet.

Experiment 6

While a porous copper sheet (thickness: 17μm, open area ratio: 24.1%) obtained in the experiment 2 was being successively transported, a paste active substance obtained by suspending a mixture of 100 parts by weight of mesophase graphite and five parts by weight of styrene butadiene rubber in an aqueous solution of carboxymethylcellulose was applied to both surfaces of the porous copper sheet and was then dried. Then, the porous copper sheet was rolled to form an electrode having a thickness of 0.2mm.

As described in experiment 6, not only an electrode of the hydrogen-storing alloy but also an electrode which is used as the negative pole of a lithium battery can be manufactured by forming a porous metal sheet which is used as an electrode substrate and supplying the active substance thereto while it is being transported successively after it is unwound or without winding it as a coil.

As apparent from the foregoing description, according to the present invention, metal powders are spread densely and directly on the feeding belt of the circulating driving device or the supporting sheet which is fed by the feeding belt, with the supporting sheet placed thereon. Then, the metal powders are rolled by rolling rollers at a required load and passed through a sintering oven to sinter the metal powders, with fine pores left between the metal powders adjacent to each other. Therefore, connected portions of the metal powders are fused together, and gaps between the metal powders adjacent to each other remain as fine pores. Therefore, a metal sheet having a large number of the fine pores can be continuously formed. It is possible to obtain a solid metal sheet, namely, a metal sheet having no pores formed thereon by setting the load of the rolling roller to a large one.

When a pore-formed sheet is used as the supporting sheet, portions corresponding to the pores are formed as through-holes. Thus, a porous metal sheet having fine pores formed between metal powders adjacent to each other and relatively large through-holes can be continuously formed.

Pores can be formed in portions where particles of sublimable fine fragments are burnt off by spreading a mixture of the sublimable fine fragments and metal powders on a feeding belt or a supporting sheet; rolling the mixture by rolling rollers at a required pressure; and removing the sublimable fine fragments. Consequently, it is possible to form three-dimensional pores having a required size and corresponding to the size of particles of the sublimable fine fragments. Accordingly, it is possible to continuously form a metal sheet having fine pores formed between metal powders adjacent to each other and comparatively large through-holes formed by the sublimation of particles of the sublimable fine fragments. Further, a porous metal sheet having pores of various sizes including through-holes can be continuously formed by using the pore-formed sheet.

As described above, it is possible to form fine pores, through-holes, and three-dimensional pores or in combination thereof. Thus, it is possible to provide an electrode substrate comprising a preferable metal sheet corresponding to the kind of a battery. That is, the

porous metal sheet of the present invention can be preferably used as an electrode substrate of a nickel hydrogen battery, a nickel cadmium battery, a lithium primary battery, a lithium secondary battery, an alkaline dry cell, a fuel cell; and an electrode plate, for example a battery for vehicles.

Further, the metal powders spread on the surface of the rolling roller or a mixture of the metal powders and the sublimable fine fragments spread thereon can be rolled at a required pressure by the rotation thereof to obtain a metal sheet having required fine pores formed thereon. The sublimable fine fragments can be burnt off in a resinous material-removing oven to form pores in the portion where the sublimable fine fragments have been present. Accordingly, it is easy to manufacture a metal sheet having pores having a desired configuration and size.

Further, a battery electrode such as an electrode of a hydrogen-storing alloy can be successively manufactured by supplying powder of an active substance such as the hydrogen-storing alloy powders to a metal sheet after it is successively formed of metal powders. That is, the present invention can enhance the productivity of an electrode outstandingly because the metal sheet and the electrode formed of the metal sheet composing the substrate thereof can be manufactured successively.

further, in the battery electrode of the present invention, because a binder is not added to the active substance consisting of powders, the amount of the active substance can be increased by that much and electricity-collecting property can be improved. More specifically, the amount of the active substance can be increased by about 7% in correspondence to the amount of the binder which is conventionally added thereto. Furthermore, electricity-collecting property can be enhanced and the performance of the battery can be improved by 5% - 10% by adding transition metal such as nickel powders or copper powders to the active substance, instead of carbon which is conventionally used as an electrically conductive material.

Claims

1. A method of manufacturing a metal sheet (10; 10") comprising the steps of:

   spreading metal powders (P) on a feeding belt (2) which is continuously fed;
   passing the feeding belt on which the metal powders have been spread through a pair of rolling rollers (15) for controlling an area of contact between the metal powders adjacent to each other by rolling the metal powders on the feeding belt at a required pressure; and
   passing the metal powders into a sintering oven (4) to fuse contact portions of the metal powders together after the rolling.

2. A method of manufacturing a metal sheet (10; 10") comprising the steps of:

   feeding a supporting sheet (20; 20'; 30) continuously;
   spreading metal powders (P) on the supporting sheet;
   feeding the supporting sheet on which the metal powders have been spread to a feeding belt (2);
   passing the supporting sheet between a pair of rolling rollers (15), together with the feeding belt for controlling an area of contact between the metal powders adjacent to each other by rolling the metal powders on the supporting sheet at a required pressure; and
   passing the metal powders into a sintering oven (4) to fuse contact portions of the metal powders together after the rolling.

3. The method according to claim 1 or 2, wherein a pressing force of the rolling roller is set to a small value to leave fine gaps (C) between adjacent metal powders rolled by the rolling roller, thereby obtaining a porous sheet with the fine gaps (C) as pores.

4. The method according to any one of claims 1 through 3, wherein sublimable fine fragments (50) which are burnt off by heating are mixed with the metal powders or spread on the feeding belt (2) or the supporting sheet (20) before the metal powders are spread thereon; a mixture of the metal powders and the sublimable fine powders spread on the feeding belt or the supporting sheet is rolled by the rolling roller (15); and after the rolling the sublimable fine fragments are burnt off in a resinous material-removing oven (23) so that the metal sheet (10") has pores (C3) which are formed in a portion where the sublimable fine fragments are burnt off.

5. The method according to any one of claims 1 through 4, wherein the feeding belt (2) forms part of a circulating driving device (1) of belt conveyor type and comprises a solid metal sheet, an inorganic sheet which may be a porous metal sheet (10; 10"), or a laminated sheet composed of the solid metal sheet and the inorganic sheet.

6. The method according to any one of claims 2 through 5, wherein the supporting sheet (20; 20'; 30) comprises an organic sheet, e.g. a solid resinous sheet, a three-dimensional reticulate resinous sheet or a porous fibrous resinous sheet, an inorganic sheet. e.g. a solid metal sheet or a porous metal sheet, or a laminated sheet composed of a plurality of such sheets.

7. The method according to any one of claims 2

through 6, wherein the supporting sheet (20) is burnt off in a resinous material-removing oven (23).

8. The method according to any one of claims 5 through 7, wherein when a porous sheet is used as the feeding belt (2) or the supporting sheet (30), and the pores (30a) of the porous sheet are circular, rhombic, polygonal or elliptic.

9. A method of manufacturing a metal sheet (10') comprising the steps of:

   spreading metal powders (P) on a surface of a pair of rolling rollers (150) rotating continuously;
   passing the metal powders between the rolling rollers for controlling an area of contact between the metal powders adjacent to each other by rolling the metal powders at a required pressure so as to form a metal sheet (10'); and
   passing the metal sheet through a sintering oven (4) to sinter the metal sheet.

10. The method according to claim 9, wherein a pressing force of the pair of rolling rollers (150) is set to a small value to leave fine gaps (C) between adjacent metal powders rolled by the rolling rollers, thereby forming a porous sheet with the fine gaps as pores.

11. The method according to claim 9 or 10, wherein sublimable fine fragments (50) and the metal powders (P) are spread on the surface of the rolling rollers; a mixture of the metal powders and the sublimable fine fragments is rolled by the rolling rollers to form the mixture into a metal sheet; and the metal sheet is passed through a resinous material removing/metal powder-sintering oven (23; 4) to burn off the sublimable fine fragments , thereby forming pores in a portion where the sublimable fine fragments are burnt off.

12. The method according to any one of claims 9 through 11, wherein a surface of at least one (150A; 150B) of the rolling rollers (150) on which the metal powders are spread is stepped at a position between a center and both edges thereof in its axial direction so that the metal powders are collected in a stepped center region (150a; 150c; 150d; 150f) thereof and pressed at a required pressure by the rolling rollers.

13. The method according to any one of claims 1 through 12, wherein after a metal sheet (10; 10'; 10") is passed through the sintering oven (4), the metal sheet is passed through a cooling oven (5).

14. The method according to claim 13, wherein the rolling, the sintering, and the cooling are repeated a plurality of times.

15. The method according to claim 13 or 14, wherein the cooled metal sheet is separated from the feeding belt (2) or the supporting sheet (20').

16. The method according to any one of claims 1 through 15, wherein metal powders are spread again on a surface of a metal sheet which is formed by the sintering, the metal powders are rolled, and then a resulting metal sheet is sintered.

17. A method of manufacturing a metal sheet, wherein pins (101) are pierced into a metal sheet (10) manufactured by a method according to any one claims 1 through 16 to form pores (10) with burrs (111).

18. The method according to claim 17, wherein, while the metal sheet is being fed, it is passed between a pair of pin-provided rollers (100A, 100B) to form the pores with burrs.

19. A metal sheet manufactured by a method according to any one of claims 1 through 18.

20. The metal sheet according to claim 19, wherein a shape of the metal sheet having pores, formed by using the sublimable fine fragments (50) or/and a porous sheet as the feeding belt (2) and the supporting sheet (30) is punching shape, reticulate shape, honeycomb shape, lath-shape, lattice-shape, expanded sheet-shape, screen-shape or lace-shape.

21. The metal sheet according to claim 19 or 20, wherein the metal sheet has lead portions (72) with less or no pores, the lead portions being spaced at predetermined intervals.

22. A substrate for a battery electrode comprising the metal sheet according to any one of claims 19 through 21.

23. An electrode for a battery in which an active substance (82) is charged into a pore of the substrate (10; 10') according to claim 22; and an active substance layer (85A, 85B) is formed on at least one surface of the substrate.

24. The electrode according to claim 23, wherein a binder is not added to the active substance (82).

25. The electrode according to claim 23 or 24, wherein the active substance (82) contains hydrogen-storing alloy powders as a main component thereof.

26. The electrode according to claim 25, wherein the active substance (82) consists of hydrogen-storing

alloy powders or a mixture of the hydrogen-storing alloy powders and a transition metal.

27. The electrode for a battery according to any one of claims 23 through 26, wherein a surface of the active substance layer (85A, 85B) is covered partly or entirely with a transition metal.

28. A battery comprising an electrode according to any one of claims 23 through 27.

Fig.1

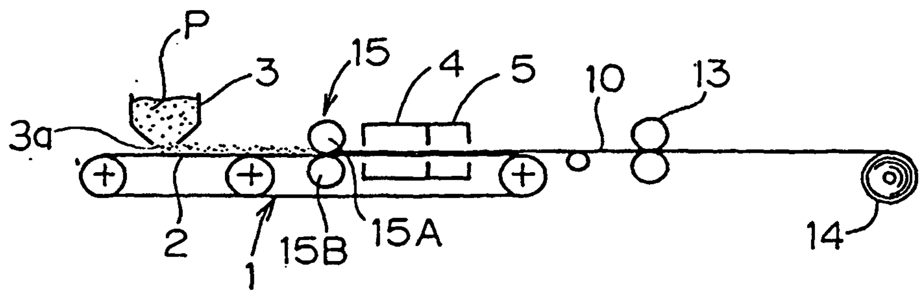


Fig.2

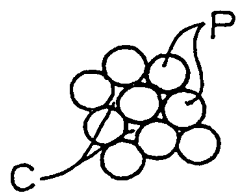


Fig.3

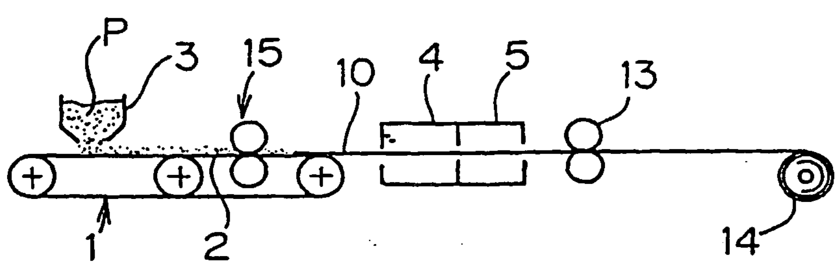


Fig. 4

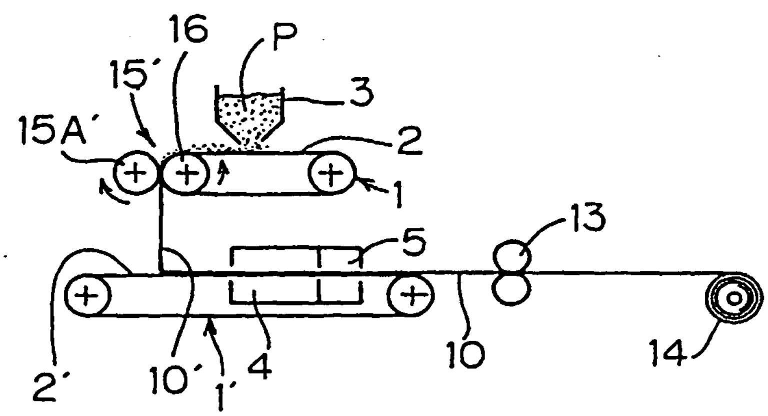


Fig.5

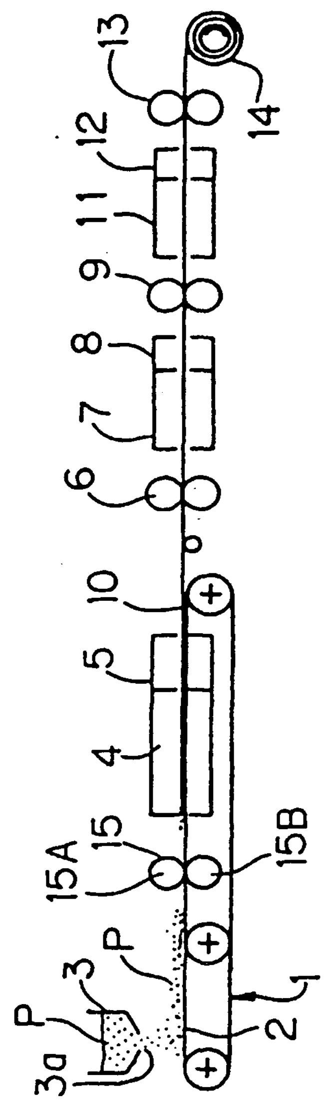


Fig.6

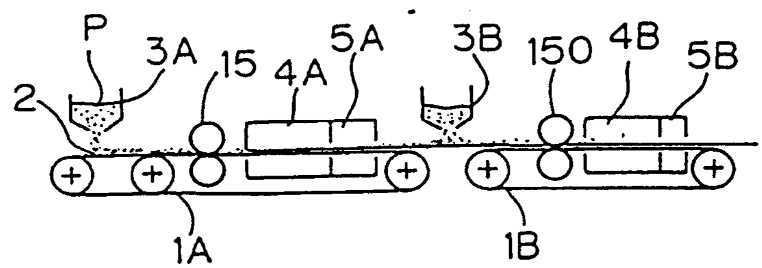


Fig.7

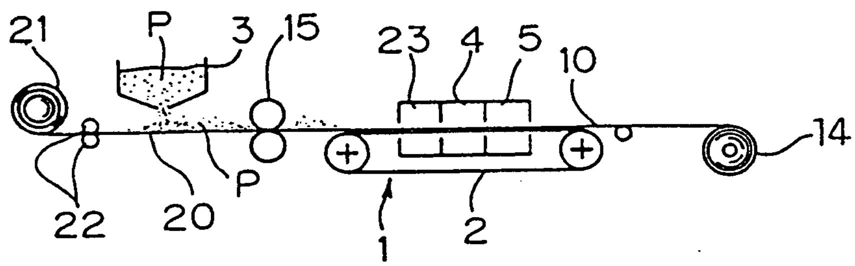


Fig.8

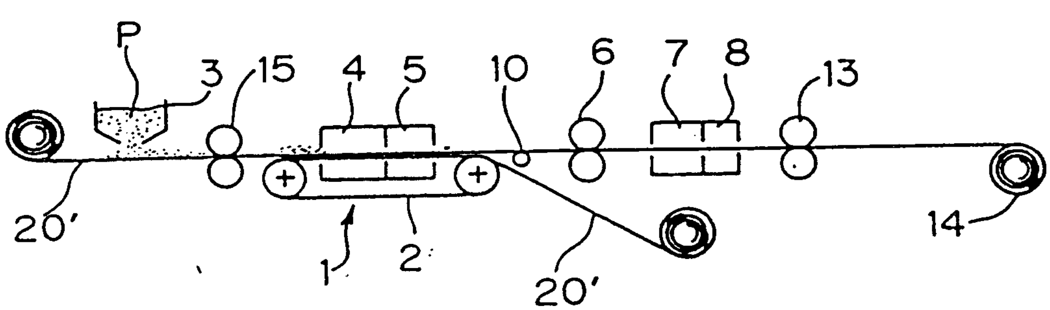


Fig.9

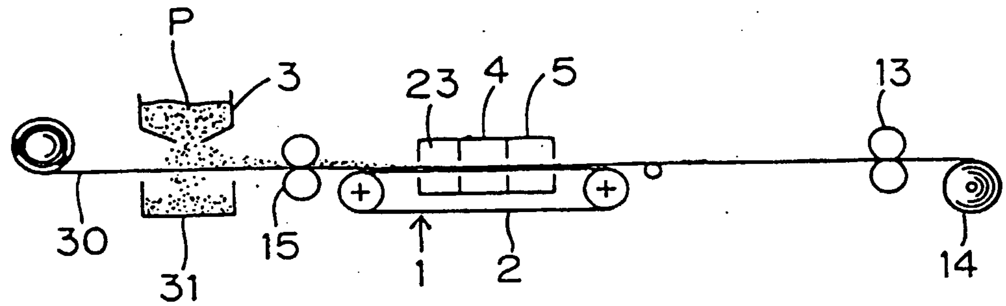


Fig.10

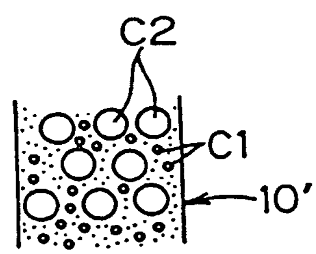


Fig.11

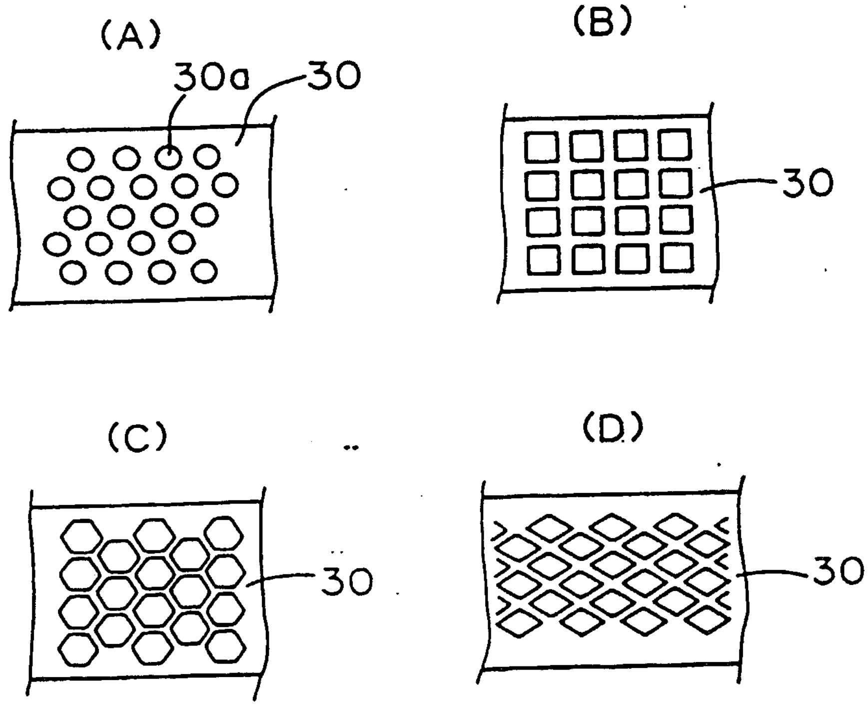


Fig.12

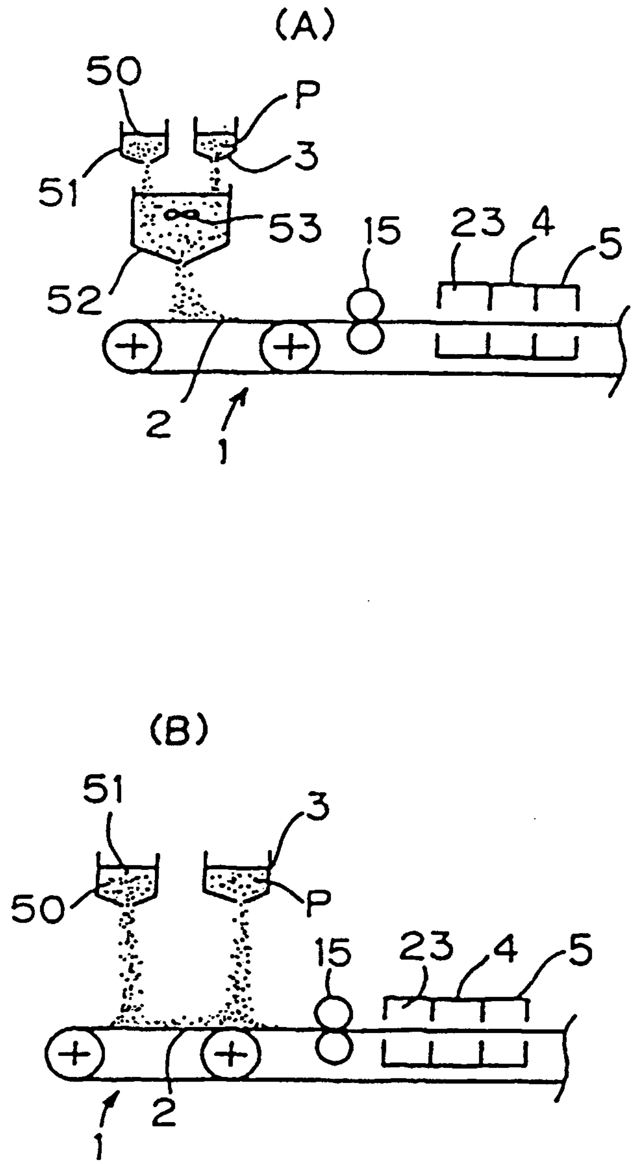


Fig.13

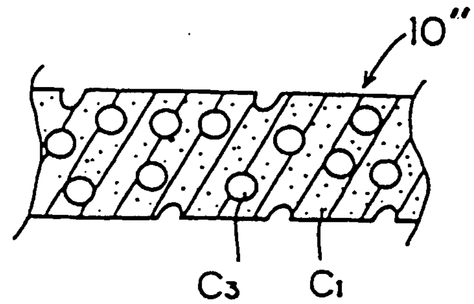


Fig.14

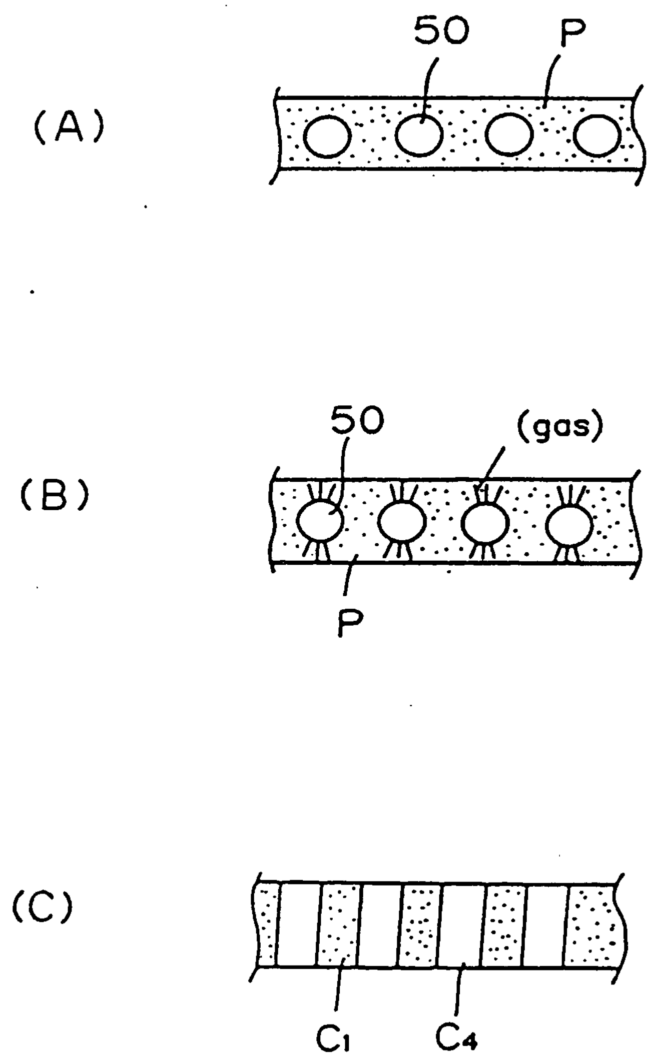


Fig.15

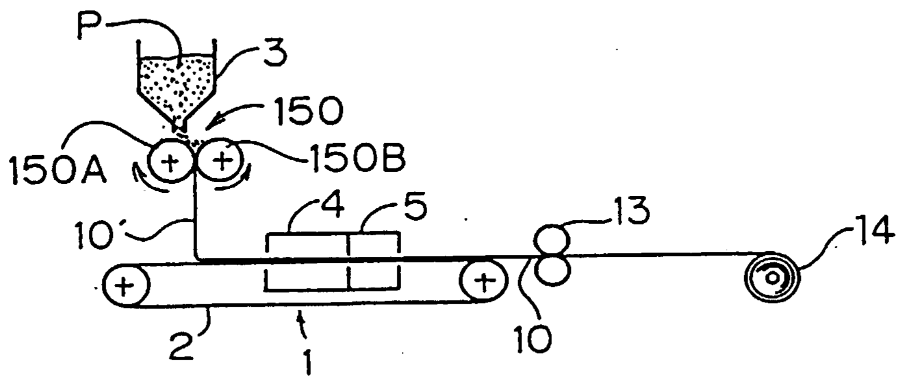


Fig.16

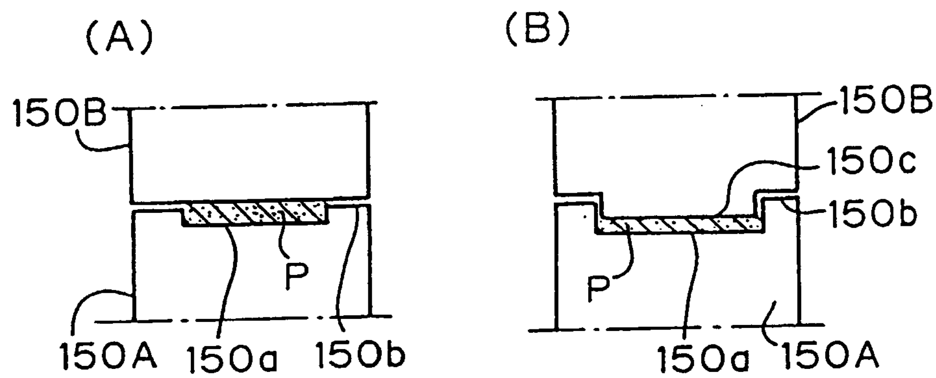


Fig.17

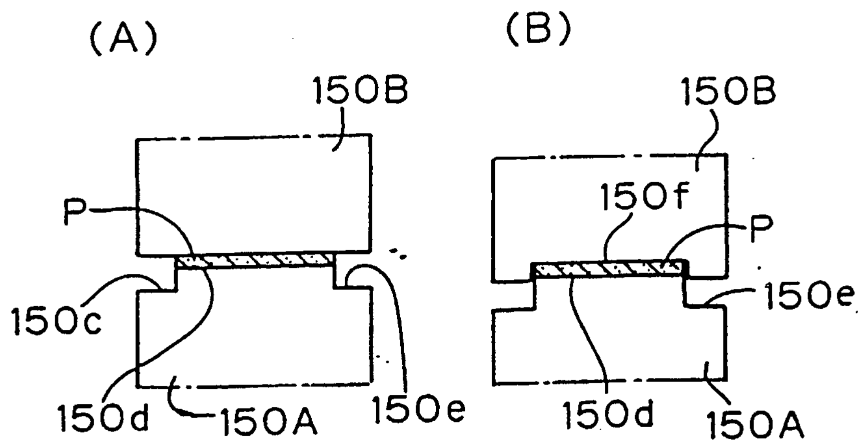


Fig.18

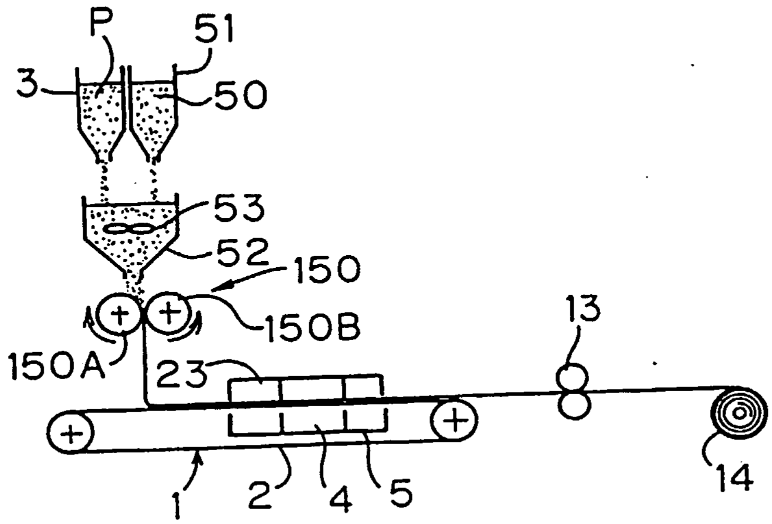


Fig.19

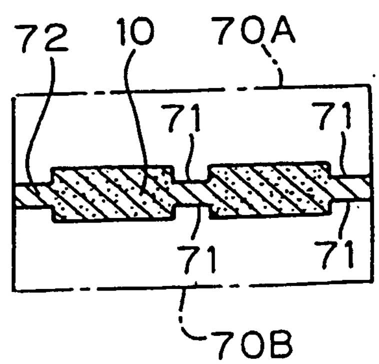
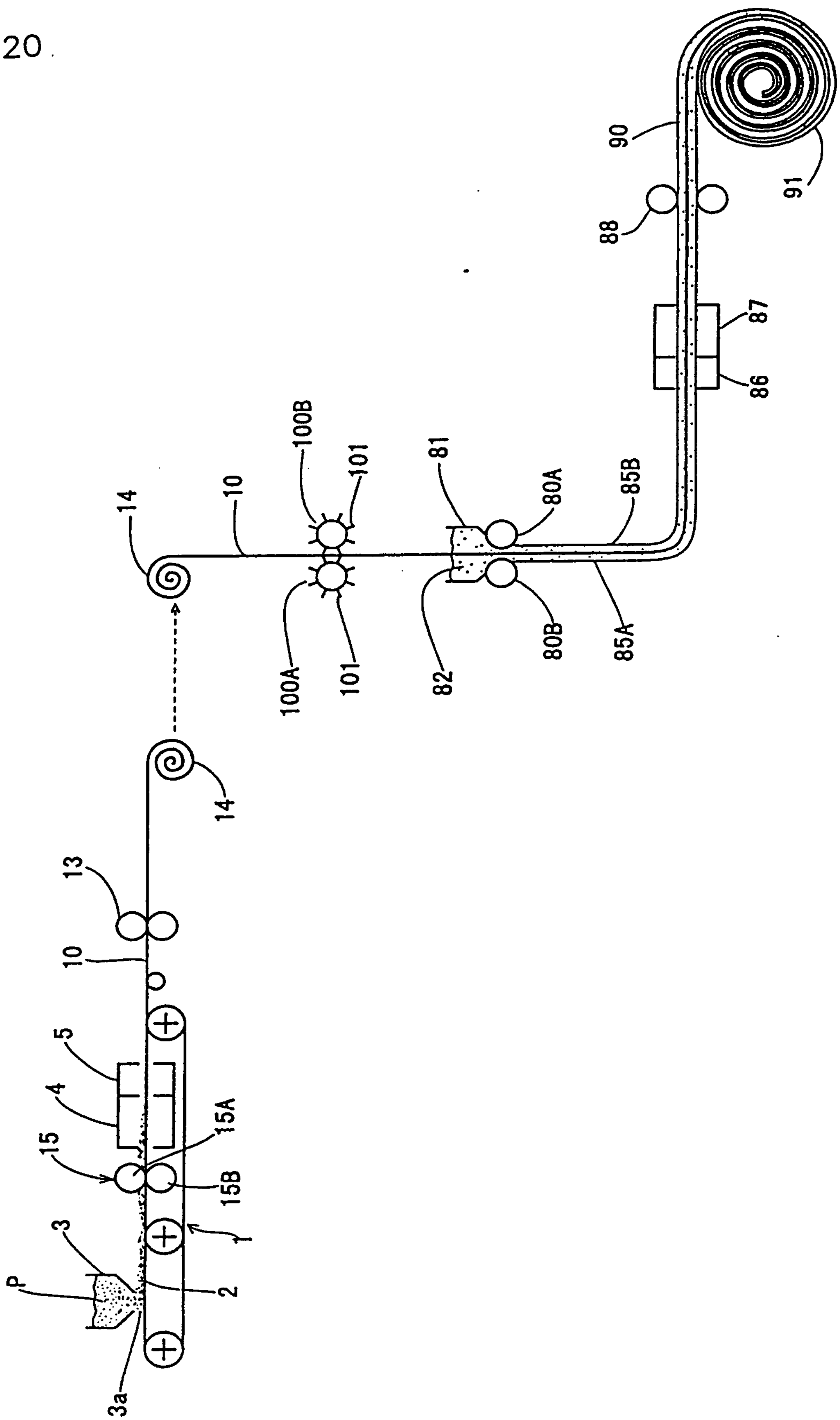


Fig.20


P
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3a
2
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15A
15B
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13
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100A
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101
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81
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80A
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85A
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Fig.23

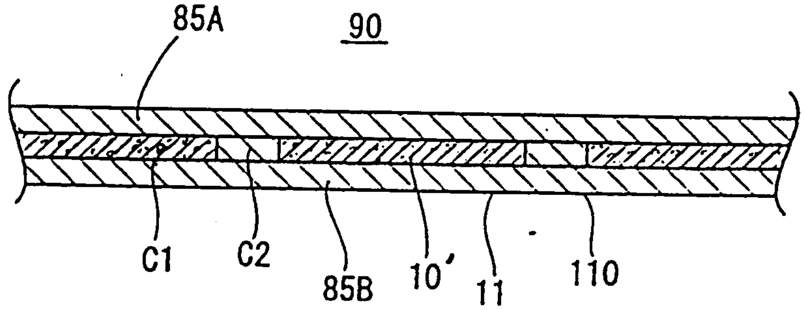


Fig.24

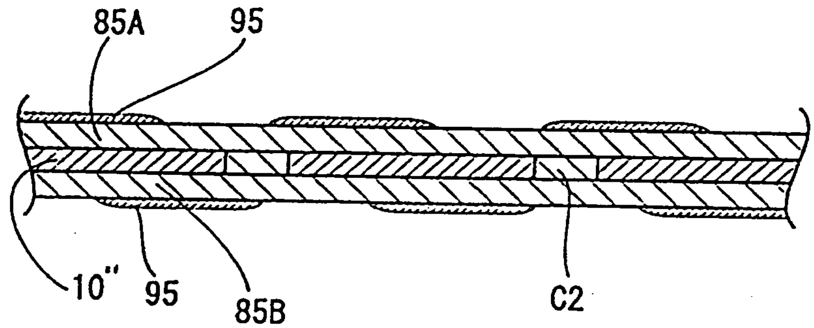


Fig.21

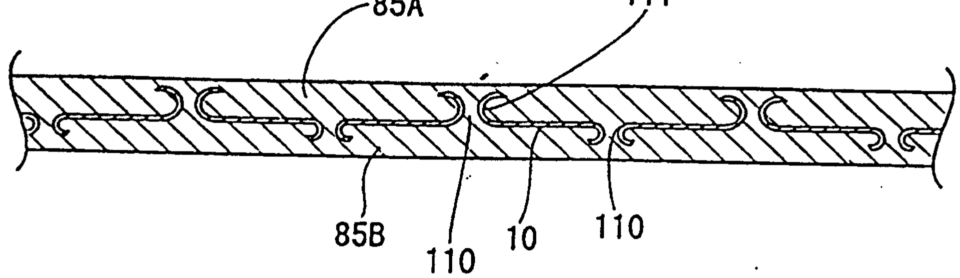
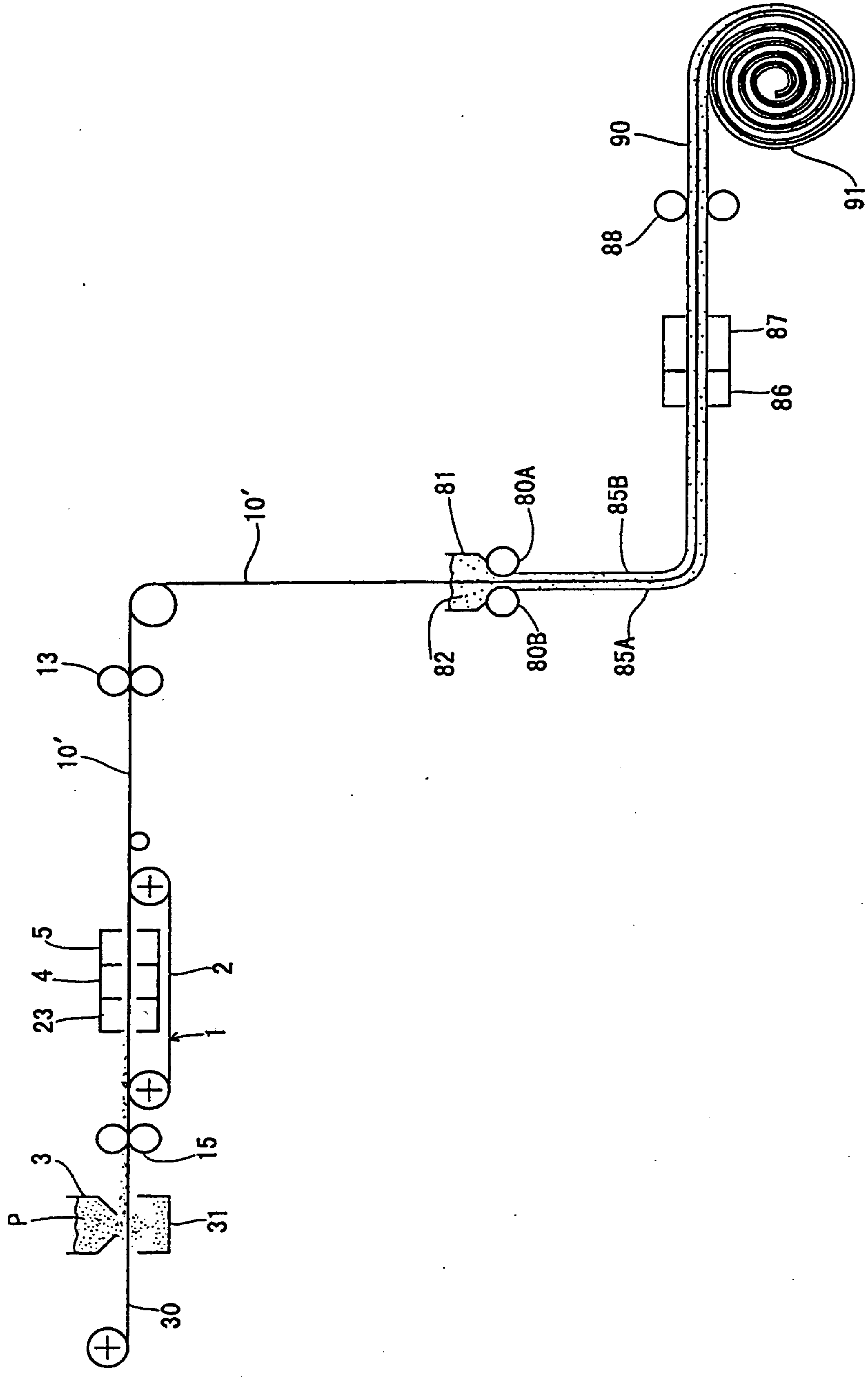


Fig.22



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 10 4931

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	FR 1 035 359 A (BADISCHE ANILIN- & SODA-FABRIK) 24 August 1953	1-3, 5-10, 12-23,28	B22F3/11 H01M4/80 H01M4/24
Y	* the whole document *	4,11	
X	EP 0 657 950 A (KATAYAMA TOKUSHU KOGYO KK) 14 June 1995 * column 6, line 8 - line 50; claims 4,6 * * column 17, line 7 - line 15 *	19-23,28	
Y	GB 1 110 852 A (VARTA A.G.) * claims 12,13 *	4,11	
A	GB 1 375 438 A (SHERRITT GORDON MINES) 27 November 1974	1-28	
A	EP 0 339 717 A (METALLGESELLSCHAFT AG ;KOLBENSCHMIDT AG (DE)) 2 November 1989 * column 3, line 34 - column 57; claims 1-7 *	1-28	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 647 973 A (SANYO ELECTRIC CO) 12 April 1995 * claims 1,2 *	25,26	B22F H01M
A	EP 0 753 896 A (AT & T CORP) 15 January 1997 * claims 1,6 *	25,27	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 July 1998	Schruers, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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